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Irradiation of ethanol solutions of coumarin laser dyes in dye lasers produces products which absorb at the lasing wavelength. This results in attenuation of dye laser output through interference of stimulated emission. A major photoprocess which produces material which absorbs at the lasing wavelength is dye sensitized solvent oxidative oligomerization, producing aldehydic and ketonic products. A dye laser stabilization technique is removal of these carbonyl compounds as they are formed by reduction with a polymer bound borohydride reducing agent.

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CHEMICAL STABILIZATION OF LASER DYES

FINAL REPORT

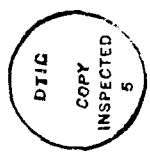
TAD H. KOCH

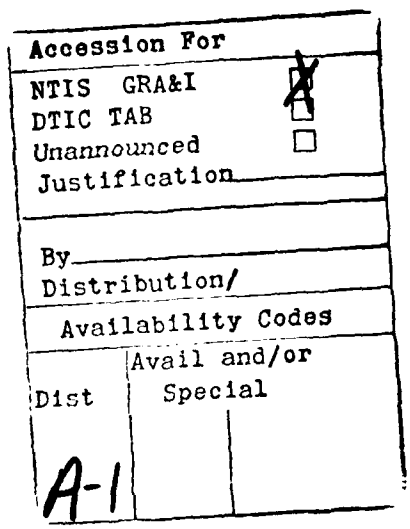
APRIL 10, 1990

U.S. ARMY RESEARCH OFFICE

DAAL03-87-K-0053

UNIVERSITY OF COLORADO





Problem Studied

Many laser dyes, especially the coumarins, are photolabile when employed in dye lasers. Products are formed which absorb at the lasing wavelength, and this absorption significantly attenuates the laser output by interfering with stimulated emission. The laser photochemistry of Coumarin 311, 7-dimethylamino-4-methylcoumarin (1), and Coumarin 360, 7-diethylamino-4-methylcoumarin (2), were studied as model systems. A major goal has been the discovery of stabilizing additives and techniques for dye lasers based upon an understanding of the photochemistry.

Summary of Important Results

a) Photobleaching. Coumarin 460, especially at 1×10^{-4} M, undergoes photobleaching upon excitation with the 308 nm XeCl excimer laser. The extent of photobleaching is a function of the radiation power flux as shown in Figure 1 suggestive of a two-photon process. The bleaching is partially reversed upon the solution standing in the presence of molecular oxygen. During the prior contract period, dye sensitized solvent oligomerization upon focused excimer laser excitation was discovered.[1] In these experiments the dye concentration was 5×10^{-3} M and very little dye was destroyed as indicated by silica gel chromatographic workup. The mechanism for solvent oligomerization was proposed to occur through simultaneous or sequential absorption of two photons by the dye followed by energy transfer to the ethanol solvent. Excited ethanol was proposed to undergo O-H and C-O bond homolyses. Subsequent radical chemistry led to the production of acetaldehyde and gaseous products such as hydrogen and butane as shown in Scheme 1. Solvent oligomers then resulted from further free radical reactions, possibly, of acetaldehyde to produce materials absorbing at the lasing wavelength of the dye. The photobleaching observed during this contract period might logically be explained by some free radical additions to the coumarin ring as shown in Scheme 2. Some of the free radical addition products would likely be susceptible to oxidation by molecular oxygen back to Coumarin 460. Free radical addition might also have occurred during the earlier experiments in which dye destruction was not observed upon chromatographic workup. In this case the silica gel chromatography might have catalyzed elimination reactions to yield back the coumarin dye. Again no simple products could be isolated or characterized from the photobleaching reaction.

b) Photosenstized production of acetaldehyde and biacetyl. Photosensitized production of acetaldehyde was proposed as a key process in the eventual production of solvent oligomers which interfered with stimulated emission. A flame ionization GLC analytical method for detection of acetaldehyde was developed. This method also revealed for the first time production of biacetyl during dye photosensitized solvent excitation. Acetaldehyde production, as expected, was a function of excimer laser focusing as shown in Table 1 and was also observed from 313 nm mercury lamp excitation of dye solutions. Consequently, acetaldehyde is also a likely product from excitation of ethanol solutions of Coumarin 460 in flashlamp pumped dye lasers.

c) Stabilization of excimer lLaser and flashlamp pumped coumarin dye lasers. Since acetaldehyde and biacetyl are reasonable key intermediates in the dye sensitized solvent oligomerization, their reduction as formed should serve to stabilize dye laser output. A strategy which has been developed is the insertion of a cartridge in the dye stream containing a polymer bound borohydride resin to reduce ketone and aldehyde functional groups to alcohol functional groups. The resin selected was a commercially avaliable poly(aminomethylstyrene) with the amino groups permethylated to make trimethylammonium groups and with the counterion borohydride. A potential added advantage for the performance of dye lasers utilizing the cartridge was the slow release of trimethylamine by the resin. The resulting low level of trimethylamine can likely function as an effective singlet oxygen quencher and free radical scavenger. As demonstrated under a previous ARO contract, singlet oxygen is continuously produced by coumarin dye lasers as molecular oxygen dissolved in the dye solution serves as a quencher of triplet dye molecules.[2] The resulting singlet oxygen possibly participates in the production of material interfering with

stimulated emission. Under a previous ARO contract, addition of 1,4-diazabicyclo[2.2.2]octane (DABCO) to an excimer pumped dye laser resulted in dye laser output stabilization, most likely from DABCO quenching of singlet oxygen and scavenging of free radicals.[3] The addition of DABCO was shown by our research group to improve the performance of excimer laser pumped dye lasers;[3] however, Fletcher and Pietrak have subsequently reported that DABCO did not improve the performance of flashlamp pumped dye lasers.[4]

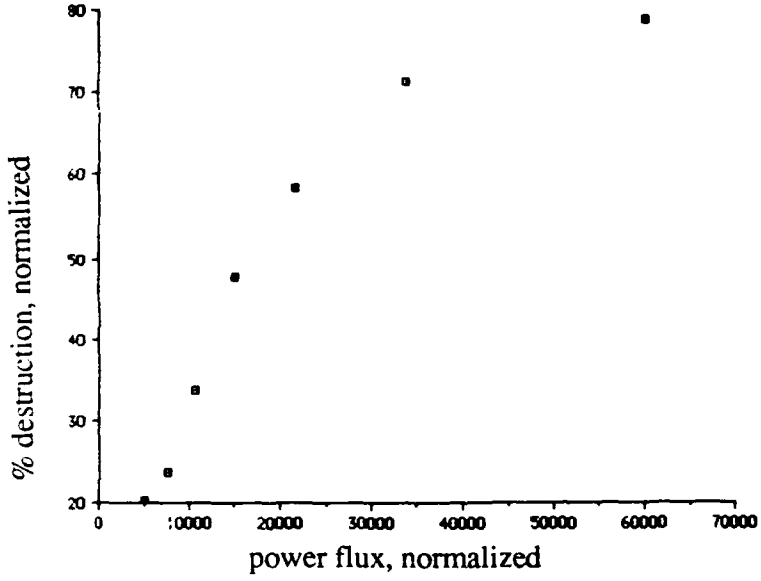
The performance of the cartridge was evaluated with a Lambda Physik EMG 101 excimer laser pumping a Lambda Physik oscillator dye cell charged with Coumarin 460 and a Phase-R Model DL-2100B flashlamp pumped dye laser charged with Coumarin 460, Coumarin 480, or LD425 (a carbostyryl dye). The excimer laser pumped dye laser was charged with 140 mL of an ethanol solution of the dye, and the flashlamp pumped dye laser was charged with 1.5 L of an ethanol solution of the dye. When Coumarin 460 and 480 dyes were flashlamp pumped, the flashlamp output was filtered with a circulating caffeine solution containing 0.5 g of caffeine / L of water. When LD 425 was flashlamp pumped no flashlamp output filtering was employed.

The effect of the cartridge containing the resin on each dye solution relative to controls is shown in Figures 2-5. The excimer laser pumped Coumarin 460 dye laser showed 25% higher output efficiency and more stable output efficiency with the cartridge in the dye stream. The output is shown as % efficiency to correct for differences in the pump power as a function of time and experiment. The flashlamp pumped Coumarin 460 dye laser showed greater than 100% more initial output power and lasing at greater than 200 mJ/pulse even to 7000 pulses with the cartridge in the dye stream. With the control, the initial power was only 140 mJ/pulse and diminished to 50 mJ/pulse in less than 500 pulses. The flashlamp pumped Coumarin 480 dye laser showed greater than 30% more initial power and lasing at greater than 250 mJ/pulse even to 6000 pulses with the cartridge in the dye stream. With the control the power again dropped to less than 50 mJ/pulse in 500 pulses. The flashlamp pumped LD 425 dye laser showed 50% more initial power and lasing at greater than 100 mJ/pulse for 1000 pulses with the cartridge in the dye stream. With the control the power dropped to less than 100 mJ/pulse in approximately 100 pulses. Consequently, with flashlamp pumped dye lasers the cartridge improved the performance by approximately an order of magnitude.

The production of acetaldehyde and the increase in the optical density of the dye laser solution at the lasing wavelength were also monitored. In general the borohydride resin lowered the concentration of acetaldehyde and the concentration of material absorbing at the lasing wavelength. These results appear in figures in a recent U. S. patent application with regard to the technology described above (manuscript included).[5]

The combination of LD425, Coumarin 460, and Coumarin 480 provide tunable light from a flashlamp pumped dye laser covering the entire region from 405 to 503 nm.

Figure 1. Normalized Percent Destruction of Coumarin 460 as a Function of Excimer Laser Power Flux at Constant Total Dose.



Scheme 1 A Mechanism for the Two-Photon Sensitized Oligomerization of Ethanol Solvent During Excimer Laser Excitation of Coumarin 460.

$$C460 \xrightarrow{h\nu} {}^1(C460)^*$$

$${}^1(C460)^* \xrightarrow{ISC} {}^3(C460)^*$$

$${}^3(C460)^* \xrightarrow{h\nu} {}^3(C460)^{**}$$

$${}^3(C460)^{**} + CH_3CH_2OH \longrightarrow C460 + {}^3(CH_3CH_2OH)^*$$

$${}^3(CH_3CH_2OH)^* \longrightarrow CH_3\dot{C}H_2 + {}^*OH$$

$${}^3(CH_3CH_2OH)^* \longrightarrow CH_3CH_2O^* + {}^*H$$

$${}^*H + CH_3CH_2OH \longrightarrow H_2 + CH_3\dot{C}HOH$$

$${}^*R + CH_3CH_2OH \longrightarrow RH + CH_3\dot{C}HOH$$

$$2\ CH_3\dot{C}H_2 \longrightarrow C_4H_{10}$$

$$CH_3\dot{C}HOH + R^* \longrightarrow CH_3CHO + RH$$

$$CH_3CHO + R^* \longrightarrow CH_3\dot{C}{=}O + RH$$

$$2\ CH_3\dot{C}{=}O \longrightarrow CH_3\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{R^*} \text{Oligomers}$$

Scheme 2. Proposed Chemistry for Photobleaching of Coumarin 460 upon Focused Excimer Laser Excitation.

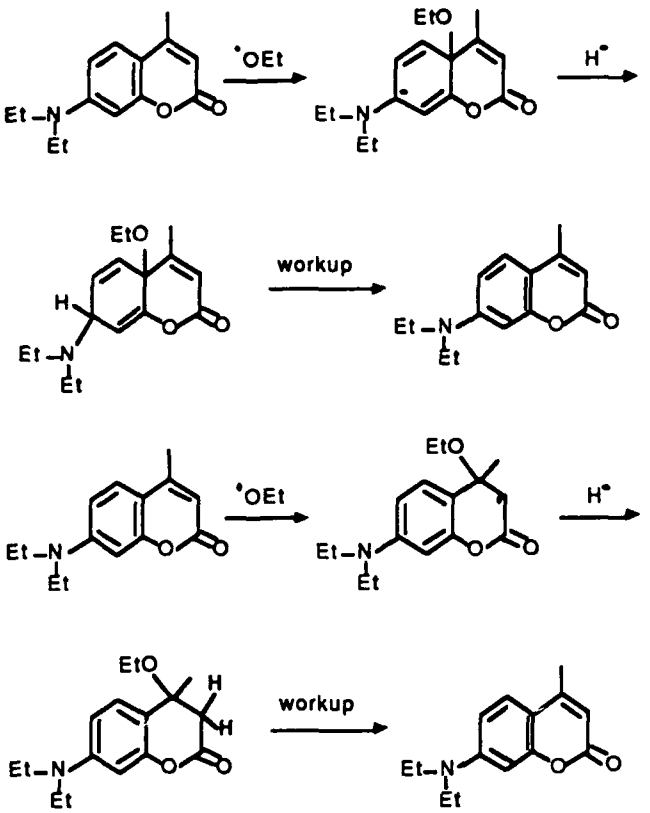


Table 1. Coumarin Dye Sensitized Acetaldehyde Production as a Function of Irradiation Conditions.

Expt. #	λ (nm)	Atmos-phere	Conditions[a]	Input (J)	Area Change CH_3CHO peak[b]
1	308	argon	laser, non-focus	88	9400→30,900
2	308	argon	laser, focus 77mm	88	7800→77,400
3	313	argon	Hg, non-focus	88	4900→10,400
6	308	argon	laser, focus 72mm	88	1800→9100
7	308	air	laser, focus 72mm	88	1700→18,300
8	308	oxygen	laser, focus 72mm	88	2400→16,600
10	308	argon	laser, focus 72mm	88	1500→10,800
12	308	argon	laser, focus 72mm	264	1000→30,500
13	308	argon	laser, focus 72mm	264	1200→43,900
14	308	argon	laser, focus 72mm	352	600→68,000

[a]The excimer laser output was focused with a 100 mm focal length spherical lens: the distance given is the distance from the spherical lens to the front window of the cell containing the dye solution. [b]The areas are the GLC peak areas for acetaldehyde at time zero and after the radiation dose. Experiments 1-3 show larger concentrations of acetaldehyde at time zero because the ethanol was not prepurified.

Figure 2. Stabilization of the output from an excimer laser pumped Coumarin 460 dye laser with the borohydride resin relative to a control. Power is reported as percent efficiency to correct for differences in excimer laser output.

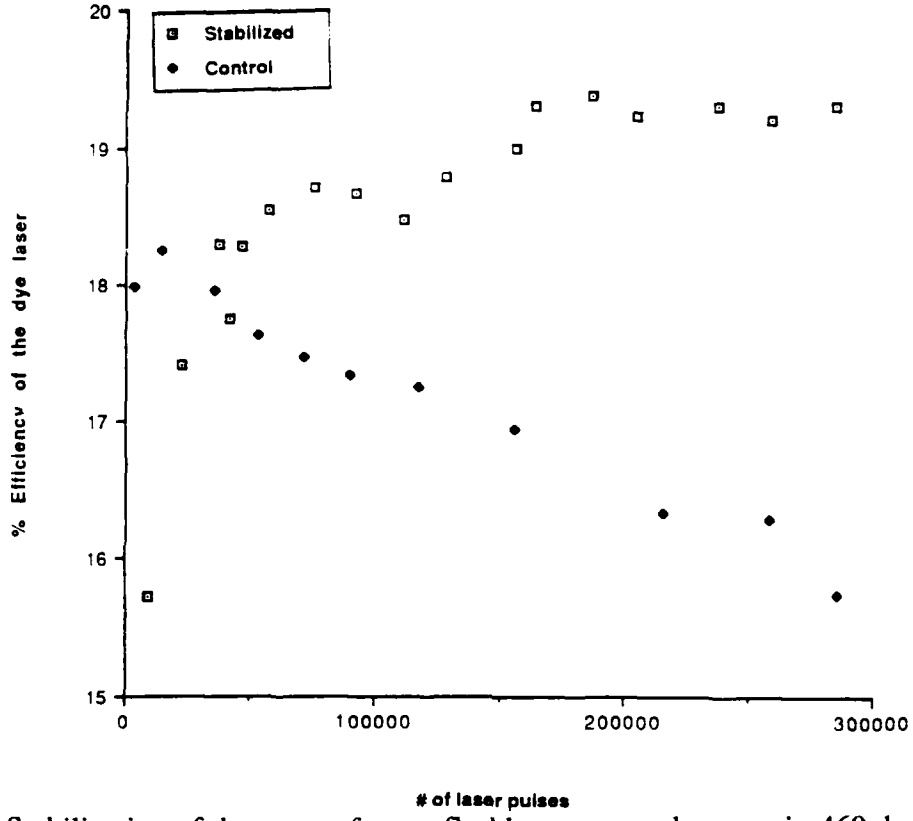


Figure 3. Stabilization of the output from a flashlamp pumped coumarin 460 dye laser with the borohydride resin relative to a control.

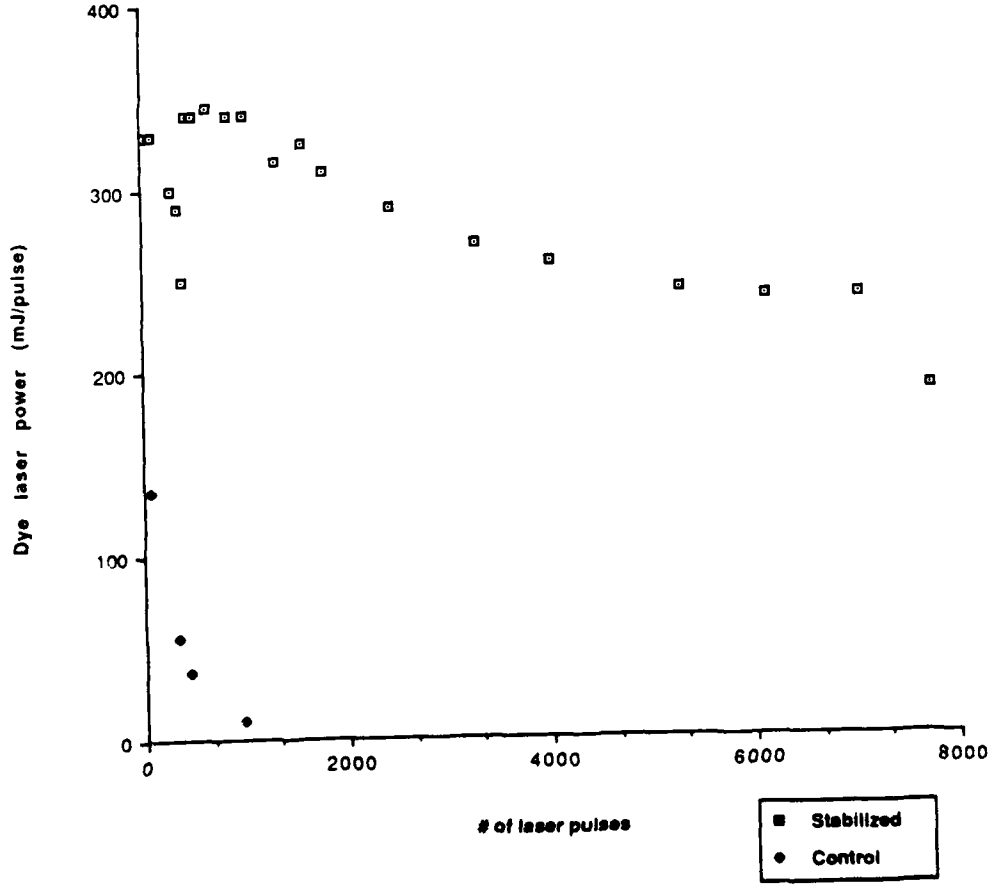


Figure 4. Stabilization of the output from a flashlamp pumped Coumarin 480 dye laser with the borohydride resin relative to a control.

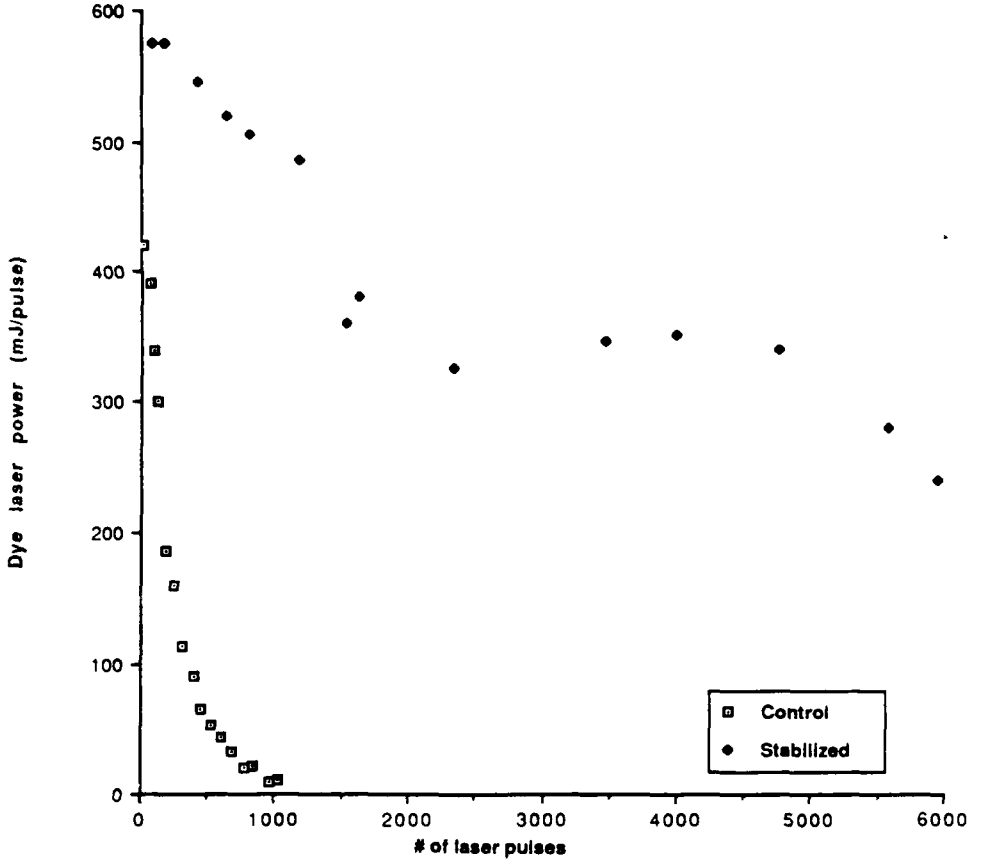
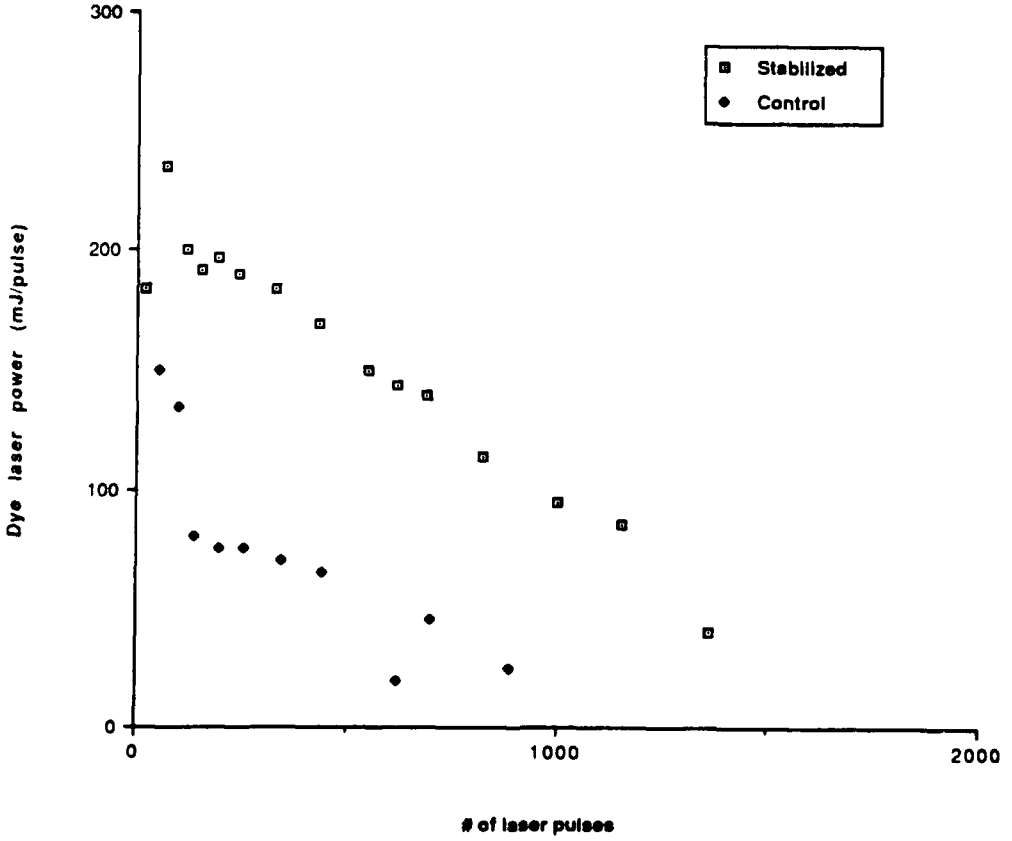


Figure 5. Stabilization of the putput from a flashlamp pumped LD 425 dye laser with the borohydride resin relative to a control.



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Participating Scientific Personnel

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Robert von Trebra, postdoctoral research associate
Timothy Dietz, graduate research assistant
Robert Mahoney, graduate research assistant

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